

# On Static Dielectric Response of Microcomposites of the Type Ferrolastics-Dielectrics For Application in Solid Oxide Fuel Cells (SOFC).

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## Abstract

We describe the static dielectric response of ferroelastic-dielectric microcomposites. Dependence on temperature, pressure and concentration is considered for temperatures in the paraelastic transition. In recent years there has been considerable interest in perovskite oxides for application in solid oxide fuel cells (SOFC), exhaust gas sensors in automobiles, membranes for separation processes and as catalysts, which are of the ferroelastic nature, f.e. of the (*LaSrCoO*<sub>3</sub>) type. Ferroelastic-dielectric microcomposites and measurement of their properties may improve properties of perovskite oxides for these applications.

# 1 Introduction

Dielectric mixtures are, [1], composites which are made up of at least two constituents. The outstanding mechanical properties of many composites, and namely the unique combination of low density with high strength and stiffness led to extensive research and to a highly developed technologies [2], [3] and [4]. In [1] attention was given to their physical properties, which affected their use in electrical applications [5], [6], [7] and [8]. In recent years there has been considerable interest in perovskite oxides for applications in solid oxide fuel cells (SOFC), exhaust gas sensors in automobiles, membranes for separation processes and as catalysts [9]. Requirements for the above materials are high electronic and ionic conductivity, stability, and satisfactory mechanical properties [10].  $LaCoO_3$  based materials are interesting for these applications due to their high electronic and ionic conductivity when La is substituted by divalent cations.  $LaCoO_3$  has a perovskite-type structure with La on A-site and Co on B-site, and the oxygen stoichiometry varies with  $O_2$  pressure and with temperature. In [10] mechanical properties of  $LaCoO_3$  based ceramics were studied. The mechanical behavior of lanthanum-cobaltite based perovskites with a mixed ion-electron conductivity at different temperatures was studied in [11], it is noted that these materials are environment-friendly. In them there are realized the direct conversion of fuel energy to electrical energy using ceramic fuel cells materials and the ion-mediated separation of oxygen from air materials. Ceramics for the above should be efficient engineering component exposed to thermal and mechanical loading conditions. They must simultaneously play the role of a structural material. Perovskites of the type  $LaCoO_3$  [12] are candidate materials for those purposes. So they are promising for fabricating membranes in the high-temperature separation of oxygen from air, the cathodes of ceramic fuel cells, etc. [13]. Ferroelastic perovskites can undergo an energy-absorbing switching rotation of ferroelastic domains [14]. The range of papers studying the mechanical behavior of perovskites is rather modest [14], for example moduli of elasticity [15], [16] strength, [17] crack resistance and other characteristics [18] and [19] have been considered.  $LaCoO_3$  as a promising cathode material for solid oxide fuel cells with a perovskite type structure has the ability to reduce itself reversibly at moderate partial pressures of oxygen, thus producing large numbers of oxygen ion vacancies. The ion vacancies allow the transport of oxygen ion and cause oxygen surface exchange, raise mechanical stress by causing volume expansion of the lattice [20]. Influence of temperature change on the properties of  $LaSrO_3$ , type LSC-82, has been reported in [21]. Effect of temperature on magnetic susceptibility has been reported [22].

In these materials behind mechanical properties also electric properties are important in relation to their mechanical properties. They are described by the dielectric susceptibility which may be studied experimentally. To improve properties of  $LaCoO_3$  based materials one may consider the ferroelastic-dielectric composites, in which  $LaCoO_3$  type material is ferroelastic. Recently we have

studied dielectric response of ferroelastic-dielectric composites for low and for high concentrations of the ferroelastic material [23] and [24]. The dielectric response of ferroelectric micro- and nano- particles and ferroelectric-dielectric type composites was studied in [25] - [34]. When a coupling of the elastic strain to the electric polarization is present then the dielectric response of a ferroelastic material may be studied, see in [35] - [36]. Also the dielectric response of ferroelastic-dielectric type microcomposites may be studied. Response of minerals to changing hydrostatic pressure  $p$  and temperature  $T$  is also interesting property of these materials. For example materials of the perovskite type ( $LaAlO_3$ ,  $CaAlO_3$ ,  $SrAlO_3$ ,  $BaTiO_3$ ,  $PbNiO_3$ ,  $Pb(Zr,Ti)O_3$ , ...) undergo a phase transition from a cubic phase to a phase with lower symmetry at some critical temperature. While a study of their elastic properties is usually done in literature, we will consider here the dielectric response of materials of ferroelastic-dielectric type which is due to coupling between the elastic strain tensor and the polarization. Mechanical analysis is usually done at low frequencies (0.1Hz - 10 Hz) but also measurements at higher frequencies are done. Ferroelastic domain wall structure, twinning and other similar phenomena are studied, see in [37] and [38]. Elastic response function (compliance) shows in Cole-Cole diagrams circular and non-circular behavior of these materials in their crystalline and ceramic form [39]. In the second case multirelaxation phenomena exist in these materials under some conditions. Under higher electric and mechanical loading nonlinear behavior is exhibited by ferroelectric and ferroelastic ceramics [40]. Coupling of the elastic strain and electric polarization does exist at these materials and thus dielectric response depends on mechanical forces acting on the composite of the ferroelastic-dielectric type. This response enables us to study properties of these microcomposites using dielectric measurements for microcomposites under mechanical forces. It is known that constraint due to neighboring material lead below the critical temperature for transition from paraelastic to ferroelastic phase and due to shape-change to several forms of the low-temperature phase [41]. As it is noted by these authors only in very small grains there exists a single variant of this form. A strain of  $10^{-4}$  in a grain of size  $10\text{ }\mu\text{m}$  (typical values) is an order of magnitude larger to be accommodated in a small displacements of atoms nearby and at surface. We assume in our paper that there are small mechanical fields of the order  $10^{-3}$  and that particles are with their diameter of the order of  $1\text{ }\mu\text{m}$ . They are microcomposites. In ferroelastic phase long-range anisotropic forces may appear [42]. In our paper we discuss properties of the microcomposite in the paraelastic phase, thus these long-range forces can be neglected. For solid oxide fuel cells namely this later limit is used. Small amount of dielectric material in ferroelastic phase (microcomposite) may improve their properties.

The aim of this paper is to study the static dielectric response of microcomposites of the type: ferroelastics-dielectrics in dependence on pressure and temperature. Both pressure and temperature play role in solid oxide fuel cells. Measuring dielectric susceptibility of ferroelastic material and of microcompos-

ites of the type ferroelastic-dielectric type one may use to change their properties. In the second chapter a model of ferroelastic-dielectric microcomposites is presented. We study the dielectric response of ferroelastic particles. Ferroelastic particles and their dielectric response to static electric field in the paraelastic limit and as a function of hydrostatic pressure is studied in the next chapter. Effective Medium Approximation (EMA) is generally used for dielectric response description of microcomposites of the type: ferroelastics-dielectrics, and then studied in low concentration limit of the dielectric material. In the last chapter we summarize our results as concerning temperature, hydrostatic pressure and concentration dependence of the dielectric material as concerning response of microcomposites of the type: ferroelastics-dielectrics.

## 2 Model of Ferroelastic-Dielectric Microcomposites

Microcomposites are composited from small particles. One of such examples are ferroelectric-dielectric microcomposites [25] - [34]. Ferroelectric properties of particles may appear in them due to presence of the polarization as a primary order parameter. An interesting possibility is to consider materials in which ferroelectricity is induced as a secondary order parameter. Primary order parameter may be the corresponding component of the elastic strain tensor. The ferroelectric state is present in such a material due to a coupling between the elastic strain tensor and the polarization. We have two types of particles in the microcomposite: ferroelastic and dielectric. Changing the concentration of these two types of particles in the microcomposite the response to external fields changes. This holds for dielectric response and for other type of responses. We are calculating in this paper the dielectric response of such a microcomposite. For simplicity we consider all particles in microcomposite of the same diameter  $d$ . In real materials there exists distribution of diameters of particles and shapes of particles. In our model we neglect this distribution for simplicity.

## 3 Ferroelastic Particles: Dielectric Response

The dielectric response of a ferroelastic particle will be studied using a Landau free energy expansion. We will assume cubic symmetry of the ferroelastic material in the paraelastic phase for simplicity. For materials of other symmetry the approach is similar. In ferroelastic materials the primary order parameter is an elastic strain tensor. Secondary order parameter is polarization. While the elastic strain tensor is coupled to the external mechanical fields (hydrostatic pressure, uniaxial stress, shear stress), the secondary order parameter is coupled to an external electric field. We will use in our calculation time and space dependent external fields in general. However for microcomposites the quasistatic

approximation for dielectric response is a convenient approximation because the wavelength of the electric field is usually much larger than the diameter of the particle. The space dependence of the external electric field may be neglected.

To find the free energy expansion we have to find invariants of the primary order parameter and of the secondary order parameter, and of primary and secondary order parameter coupled. In cubic materials there are the following invariants from the components of the elastic strain tensor, the primary order parameter,  $\epsilon_{i,j}$  where  $i, j = 1, 2, 3$  denotes axis of the cubic material (Einstein sum rule is used)

$$\epsilon_{i,j}\epsilon_{j,i} = 3\epsilon^2 + 6\phi^2 \quad (1)$$

which is of the second order in the elastic strain tensor, and

$$\epsilon_{i,j}\epsilon_{j,k}\epsilon_{k,i} = 3\epsilon(\epsilon^2 + 2\phi^2) + 6(2\epsilon\phi + \phi^2)\phi. \quad (2)$$

This term is of the third order in the elastic strain tensor. Here we denoted on-diagonal terms in  $\epsilon_{k,i}$  as  $\epsilon$  and off-diagonal terms of the elastic strain tensor  $\epsilon_{k,i}$  as  $\phi$  for the cubic phase.

The coupling between the primary order parameter (elastic strain tensor) and the secondary order parameter (electric polarization) is of the first order in the elastic strain tensor and of the second order in the polarization. We will consider in the free energy expansion only these two invariants for the elastic strain tensor described above, (1) and (2). Thus in the corresponding to polarization part of the free energy expansion there will be the second order term, the fourth order terms and the sixth order terms in general.

The coupling between the elastic strain tensor  $\epsilon_{k,i}$  and the polarization vector  $P_i$  has the form

$$\epsilon_{i,j}P_iP_j = \epsilon P^2. \quad (3)$$

The polarization vector  $P_i$  is assumed to have a nonzero component only in the x-direction, we assume that external electric field will be applied in this direction. Then the free energy  $F$  expansion has the form

$$F = \int dV \left[ \frac{B}{2}(\epsilon^2 + 2\phi^2) + \frac{C}{3}(\epsilon(\epsilon^2 + 2\phi^2) + 2(2\epsilon\phi + \phi^2)\phi) + \Gamma P^2\epsilon + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 - E.P - \epsilon_{i,j}\sigma_{j,i} \right]. \quad (4)$$

The last term in the free energy expansion depends on the stress tensor. This tensor may be hydrostatic pressure  $p$ , then  $\sigma_{j,i} = \delta_{j,i}p$ , uniaxial stress  $\sigma_{x,x} = \sigma$  or shear stress  $\sigma_{x,y}$ . The constants in the free energy expansion (4) are positive and temperature independent, with the exception of the constant  $B$ , for which  $B = B_0(T - T_c)$  where  $B_0$  is a constant,  $T_c$  is a critical temperature

for the transition from the paraelastic to the ferroelastic phase. The expansion constants in (4) may be in fact temperature and hydrostatic pressure dependent. We will not consider this dependence with the exception of the constant B. Depending on the field applied (electric, mechanical) we calculate the response of the material described by the free energy expansion (4). We will assume that the surface charge is compensated in the case of polarized particles, and surface effects are neglected for the strain.

Let us now consider the paraelastic phase. In this case the free energy expansion from (4) takes the form in which second order and fourth order terms in the polarization are taken into account and the first order terms in the elastic strain tensor are taken into account. Note that the second order in the electric polarization is corresponding to the first order in the elastic strain tensor. However the coupling term is of the fourth order in polarization, so also the second order term in elastic strain tensor is taken into account. Then the free energy  $F$  expansion has the form

$$F = \int dV \left[ \frac{B}{2}(\epsilon^2 + 2\phi^2) + \Gamma P^2 \epsilon + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 - E.P - \epsilon_{i,j} \sigma_{j,i} \right]. \quad (5)$$

Let us consider the static case of the electric field and of the hydrostatic pressure in the following section.

## 4 Dielectric Response of Ferroelastic Particles: Static High Temperature Limit and Hydrostatic Pressure Dependence

In this case the free energy expansion (5) has the form:

$$F = \int dV \left[ \frac{B}{2}(\epsilon^2 + 2\phi^2) + \Gamma P^2 \epsilon + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 - E.P - 3\epsilon p \right]. \quad (6)$$

Here  $p$  is the hydrostatic pressure. The Lagrange-Euler equations for the most stable state at a given electric field and hydrostatic pressure have the form

$$\begin{aligned} B\epsilon - 3p + \Gamma P^2 &= 0 \\ \alpha P + \beta P^3 + 2\Gamma \epsilon P - E &= 0 \\ \phi &= 0. \end{aligned} \quad (7)$$

We obtain that the dielectric permittivity  $\epsilon_f$  has the form

$$\epsilon_f = \frac{1}{\alpha^*} \equiv \frac{1}{\alpha} \left( \frac{1}{1 + \frac{6\Gamma p}{B\alpha} + \left( \frac{\beta}{\alpha} - \frac{2\Gamma^2}{B\alpha} \right) P^2} \right) \quad (8)$$

When the condition

$$(\alpha + \frac{6\Gamma p}{B})^2 \gg \left| \beta - \frac{2\Gamma^2}{B} \right| E^2 \quad (9)$$

is fulfilled, e.i. for small electric field  $E^2 \ll \frac{(\alpha + \frac{6\Gamma p}{B})^2}{\left| \beta - \frac{2\Gamma^2}{B} \right|}$  for given temperature, pressure  $p$  and constants  $\alpha$ ,  $\beta$ ,  $\Gamma$ ,  $B_0$  and  $T_c$ , then the dielectric permittivity  $\epsilon_f$  has the form

$$\epsilon_f = \frac{1}{\alpha^*} \equiv \frac{1}{\alpha} \left( \frac{1}{1 + \frac{6\Gamma p}{B\alpha}} \right) \quad (10)$$

The dielectric constant  $\frac{1}{\alpha}$  is  $\left( \frac{1}{1 + \frac{6\Gamma p}{B\alpha}} \right)$  times changed than that in zero pressure case. We assume that  $B > 0$  and that  $B = B_0(T - T_c)$ . Taking higher harmonics  $\frac{\beta}{4}P^4$  in the free energy expansion into account we obtain that the dielectric permittivity  $\epsilon_f^* \equiv \frac{1}{\alpha^{**}}$  has approximately the form

$$\epsilon_f^* = \frac{1}{\alpha^{**}} \equiv \frac{1}{\alpha} \frac{1}{\left( 1 + \frac{6\Gamma p}{B\alpha} + \left( \frac{\beta}{\alpha} - \frac{2\Gamma^2}{B\alpha} \right) \left( \frac{1}{\alpha^*} E \right)^2 \right)} \quad (11)$$

Here we have taking  $P \approx \frac{1}{\alpha^*} E$  in (8). The term  $P^2$  in (11) may be neglected for small fields  $E$  and then we obtain from (11) the form (8). As we can see from the equation (11) the dielectric permittivity may behave differently now with increasing hydrostatic pressure, and is electric field  $E$  dependent.

## 5 Effective Medium Approximation-General Formulation for Dielectric Response of Composites of the Type: Ferroelastics-Dielectrics

The effective permittivity  $\epsilon_{eff}$  may be obtained, [25], from the effective medium approximation for the whole interval of concentrations  $0 \leq x \leq 1$  of the dielectric components of the ferroelastic-dielectric microcomposite

$$x \frac{\epsilon_d - \epsilon_{eff}}{\epsilon_d + 2\epsilon_{eff}} + (1 - x) \frac{\epsilon_f - \epsilon_{eff}}{\epsilon_f + 2\epsilon_{eff}} = 0 \quad (12)$$

This approximation is based on the response of a spherical particle to the whole effective microcomposite. Both components of the microcomposite are taken into account symmetrically. For the permittivity of the hard dielectric material we take the constant dielectric permittivity  $\epsilon_d$  and for the permittivity of the ferroelastic material  $\frac{1}{\alpha} \frac{1}{(1 + \frac{6\Gamma p}{B\alpha})}$ . The effective permittivity calculated from (12) will describe dielectric response of the microcomposite on the electric field and on the hydrostatic pressure. Let us now consider the limiting case: the limit of small concentration of the hard dielectric material.



## 6 High Concentration of the Ferroelastic Material

For low concentration of dielectric particles in the ferroelastic matrix we may calculate the dielectric response of the microcomposite from (12). In this case we have  $x$  near the value 0. The value  $x = 0$  corresponds to ferroelastic material only. Thus  $x$  is a small parameter now. The effective dielectric permittivity  $\epsilon_{eff}$  is given as

$$\epsilon_{eff} = \epsilon_f + 3x\epsilon_f \frac{\epsilon_d - \epsilon_f}{\epsilon_d + 2\epsilon_f} \quad (13)$$

Substituting for the ferroelastic permittivity from (8), where we neglect the term  $P^2$ , we obtain hydrostatic pressure, temperature and concentration dependence of the effective dielectric permittivity in the cubic phase of ferroelastic matrix with dielectric material in this limit as

$$\begin{aligned} \epsilon_{eff} = & \frac{1}{\alpha} \frac{1}{(1 + \frac{6\Gamma p}{B\alpha})} + \\ & + 3x \frac{1}{\alpha} \frac{1}{(1 + \frac{6\Gamma p}{B\alpha})} \cdot \frac{\epsilon_d - \frac{1}{\alpha} \frac{1}{(1 + \frac{6\Gamma p}{B\alpha})}}{\epsilon_d + 2 \frac{1}{\alpha} \frac{1}{(1 + \frac{6\Gamma p}{B\alpha})}} \end{aligned} \quad (14)$$

As we can see for dielectric material with  $\epsilon_d$  such that  $(\epsilon_d - \frac{1}{\alpha} \frac{1}{(1 + \frac{6\Gamma p}{B\alpha})}) > 0$  we may increase the effective dielectric response of the microcomposite by the hard dielectric material. This may influence oxygen and electron particles in their move in the material.

The response of the diagonal component  $\epsilon_{elastic,f}$  of the elastic strain tensor, neglecting the term  $P^2$ , has the form of the Hook law

$$\epsilon_{elastic,f} = \frac{3p}{B} \quad (15)$$

for the ferroelastic material in the paraelastic phase. For the microcomposite in this limit we obtain

$$\epsilon_{elastic,eff} = \frac{3p}{B} + 3x \frac{3p}{B} \frac{\epsilon_{elastic,d} - \frac{3p}{B}}{\epsilon_{elastic,d} + 2 \frac{3p}{B}}. \quad (16)$$

Here  $\epsilon_{elastic,d}$  is the diagonal component of the elastic strain tensor of the dielectric material. For  $p_c = \epsilon_{elastic,d} \frac{B}{3}$  the contribution of the dielectric component in the microcomposite to the response  $\epsilon_{elastic,eff}$  changes the sign for nonzero concentration  $x$  as can be seen from

$$\epsilon_{elastic,eff} = \frac{3p}{B} + 3x \frac{3p}{B} \frac{\frac{p_c}{p} - 1}{\frac{p_c}{p} + 2}. \quad (17)$$

## 7 Summary

We studied here the static dielectric response of microcomposites: ferroelastic-dielectric. A model for such a microcomposite was formulated. Dielectric properties of ferroelastic particles were studied. We considered a coupling of the elastic strain tensor to the electric polarization. While the primary order parameter is coupled to external mechanical fields, the secondary order parameter is coupled to external electric field. We have found the free energy expansion using invariants of the primary order parameter, of the secondary order parameter, and of their mixed terms. We assumed that in the free energy expansion only the coefficient  $B$  of the second order of the primary order parameter is temperature dependent, and that other parameters are temperature independent. All of these coefficients are assumed to be hydrostatic pressure independent. Surface charges are assumed to compensate the dipole moment in ferroelastic particles in which an electric dipole appears. We apply hydrostatic pressure on the microcomposite and consider properties of such a microcomposite here. The most important role in the free energy expansion plays terms of the second order in the elastic strain tensor and of the second order in electric polarization. The fourth order terms of the polarization are small for small electric fields and we do not consider them here. We studied the dielectric response of the ferroelastic particles for paraelastic phase and its hydrostatic pressure dependence.

The dielectric response of a particle is depending on hydrostatic pressure: increasing hydrostatic pressure the dielectric response is smaller for the constant  $\Gamma$  positive and larger for the constant  $\Gamma$  negative (we assume  $(1 + \frac{6\Gamma p}{B\alpha}) > 0$ ).

The effective medium approximation theory is formulated for study of the dielectric response of the microcomposite. The limit of small concentrations of the hard dielectric material is studied here and the effective dielectric constant is calculated. Increasing temperature the effective dielectric constant of the microcomposite the dielectric response of the microcomposite is tending to the dielectric response of the microcomposite which is under no hydrostatic pressure.

The low concentration of the dielectric material increases the effective permittivity of the microcomposite with nonzero hydrostatic pressure for dielectric material with  $\epsilon_d$  such that  $(\epsilon_d - \frac{1}{\alpha} \frac{1}{(1 + \frac{6\Gamma p}{B\alpha})}) > 0$ .

In our model above we did not consider the mechanical inclusion/matrix interactions. We discuss temperatures in which there is the paraelastic phase. Effect of elastic clamping was not considered here. For its discussion for an improper and a pseudoproper ferroelastic inclusion see [43]. For ellipsoidal shapes of the ferroelastic inclusions the order parameter and strain are uniform inside the inclusion. For improper and pseudoproper ferroelastic inclusions and polycrystalline inclusion/matrix interaction renormalizes the constant of the Landau free energy expansion of the order parameter. For proper ferroelastic materials which we consider here 3D clamping of the crystal inclusion in the matrix is not considered, we assume the mechanical equilibrium of the inclusion/matrix

system is present at temperatures considered. As concerning crystal structure of perovskite  $La_{1-x}Sr_xCoO_3$  for  $0.0 < x < 0.7$  it was studied by [44]. The space group was assigned to rhombohedral  $R\bar{3}c$  in the range  $0.0 < x < 0.5$  and to cubic  $Pm\bar{3}m$  in the range  $0.55 < x$ .

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